

ACCUMULATION OF RARE EARTH ELEMENTS, U AND Th IN FLOATING MACROPHYTES FROM THE GUARAPIRANGA RESERVOIR

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ABSTRACT

Macrophytes play a relevant role in aquatic environments since they may accumulate metallic elements and can be an important tool for bioaccumulation studies, especially concerning an important and strategic water supply as Guarapiranga Reservoir. The reservoir is one of the main water supply systems in the São Paulo Metropolitan Region, contributing with 20% of the water provided to the region, which represents a water supply for about 3.7 million people. The industrial use of rare earth elements (REEs) has increased in the last years, affecting the levels of REEs in urban environments. Information about REEs accumulation in macrophytes of reservoirs are scarce, and none for Guarapiranga Reservoir. This study aims to evaluate REEs, U and Th concentration in floating macrophytes of Guarapiranga Reservoir, in order to assess possible sources and potential environmental impacts. Sampling was performed with the support of the Environmental Agency of the state of São Paulo (CETESB) in three points along the reservoir for dry (September 2016) and wet season (March and April 2016). Macrophyte samples were analyzed by Instrumental Neutron Activation Analysis (INAA) for REEs and Th and by Inductively Coupled Plasma Mass Spectrometry (ICP MS) for U. The results obtained were compared to Guarapiranga soil values and to other study using floating macrophytes, indicating a natural source of these elements in Guarapiranga Reservoir.

1. INTRODUCTION

Rare earth elements (REEs) are a group of seventeen strongly related chemical elements that comprise the lanthanide series (lanthanum – ⁵⁷La, cerium – ⁵⁸Ce, praseodymium – ⁵⁹Pr, neodymium – ⁶⁰Nd, promethium – ⁶¹Pm, samarium – ⁶²Sm, europium – ⁶³Eu, gadolinium – ⁶⁴Gd, terbium – ⁶⁵Tb, dysprosium – ⁶⁶Dy, holmium – ⁶⁷Ho, erbium – ⁶⁸Er, thulium – ⁶⁹Tm, ytterbium – ⁷⁰Yb and lutetium – ⁷¹Lu) plus scandium (²¹Sc) and yttrium (³⁹Y). They have similar chemical properties and are commonly divided into two groups: light rare earth elements (LREEs) that include the lower atomic weight elements lanthanum to samarium, with atomic numbers 57 to 62 (La, Ce, Pr, Nd, Pm and Sm) and the heavy rare earth elements (HREEs), which are formed by europium to lutetium, with atomic numbers 63 to 71 (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) [1-2].

Lanthanides have been used more and more for industrial purposes, and, nowadays, these elements can be found in several industrial branches, such as metallurgical additives, chemical catalysts, electronic components in cell phones and flat panel displays, automotive catalytic converters, glass polishing and ceramics, permanent magnets, among other applications [3].

The increased use of REEs in different industrial sectors is very concerning because it leads to the introduction of REEs to the environment with unknown implications to biota, affecting the levels of these elements in urban environments, which would disturb the aquatic system and also plant and soil ecosystem [1;4]. Regarding to aquatic systems, almost all human activities can be considered potential pollutants sources and these substances enter the aquatic system via numerous pathways, including effluent discharge, industrial, urban and agricultural run-off and even airborne deposition [5].

Once in the environment, pollutants can be uptaken for aquatic organisms from water, air, soil and sediment. These organisms are used as aquatic pollution bioindicators, in order to investigate aquatic pollution degree [6]. Macrophytes play a relevant role in aquatic environments once they accumulate metallic elements and can be a suitable tool for environmental studies, mainly concerning an important and strategic water supply as Guarapiranga Reservoir.

Guarapiranga Reservoir is one of the most important water supply systems in the São Paulo Metropolitan Region, contributing with 20% of the water provided to the region, which represents a water supply for about 3.7 million people. This reservoir presents many pollution related problems, which is caused especially due to untreated sewage discharge and diffuse pollution [7-8]. Nowadays, there are still few data on REEs, U and Th accumulation in macrophytes of reservoirs and none for Guarapiranga Reservoir. Thus, this study aims to evaluate REEs, U and Th concentration in floating macrophytes of Guarapiranga Reservoir, in order to assess possible sources and potential environmental impacts.

2. MATERIALS AND METHODS

2.1. Sampling and Sampling Preparation

Macrophytes samples were collected in March, April and September 2016 (wet and dry season, respectively) in three consecutive weeks during two sampling campaigns at three sites along the reservoir. Sampling was conducted with the support of the Environmental Agency of the State of São Paulo (CETESB). The locations of the three sites are presented in Fig. 1 and the geographical positions and description of each sampling site are presented in Table 1.

Four species of floating macrophytes were collected: *Eichhornia crassipes* (Mart.) Solms. *Pistia stratiotes* L. *Salvinia herzogii* de la Sota and *Salvinia cf molesta* D. S. Mitch. They were chosen according to their abundances and plant cover. Macrophytes samples (at least five plants of each specie) were collected by hand and placed in plastic bags after species identification using image bank provided by literature [9-10]. The plants were not washed on-site.

Composite macrophytes samples were dried within paper bags at $40^{\circ}\text{C} \pm 2^{\circ}\text{C}$ in a ventilated oven until constant weight, finely ground using a GM200 knife mill (Retsch, Germany), and then 0.5g of each sample and certified reference material were digested with nitric acid, hydrofluoric acid and boric acid using an Ethos microwave digestion oven (Milestone, Italy) before determination [11].

2.2. Chemical Analysis

Digested macrophyte samples were analyzed for U by Inductively Coupled Plasma Mass Spectrometry (ICP MS) using a Xseries 2 (Thermo Scientific, USA). Analytical quality control was performed by certified reference material Peach leaves (SRM 1547 NIST) analysis. The coefficient of variation presented a deviation between replicates below 10% and bias lower than 5%.

Instrumental Neutron Activation Analysis (INAA) was applied to macrophyte sample analysis to assess the levels of REEs (La, Ce, Nd, Sm, Eu, Yb and Lu) and Th. Approximately 150 mg of dried and ground plant samples were irradiated under a thermal neutron flux of 3 to 5×10^{12} $\text{n cm}^{-2} \text{s}^{-1}$ for 8 hours. The irradiation was carried out at the IEA-R1 nuclear research reactor at the Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN), Brazil. The counting system acquisition was constituted by a Canberra hyperpure germanium detector with a full-width at half-maximum (FWHM) resolution of 1.90 keV at 1332 keV. The Vispect software was used for spectra processing and peak area determinations. The comparative method was applied to calculate element concentrations using two certified reference materials (INCT tea leaves - TL1 and mixed polish herbs – MPH2). The precision and accuracy of the data were assessed by the analysis of the certified reference material Peach leaves (SRM 1547 NIST). The results showed relative errors lower than 10%. Z score values assured all results in the 95 % confidence interval.

Table 1: Description and geographical positions of the sampling sites

Site	Location	W	S
S-01	Tributary of the Embu-Guaçu River, about 2 km upstream of the Rodoanel bridge	46°47'12"	23°46'32"
S-02	In the middle of the Parelheiros River tributary, in the Balneário São José neighborhood	46°43'37"	23°45'15"
S-03	Left shore next to the SABESP's water catchment point in the reservoir	46°43'40"	23°40'27"

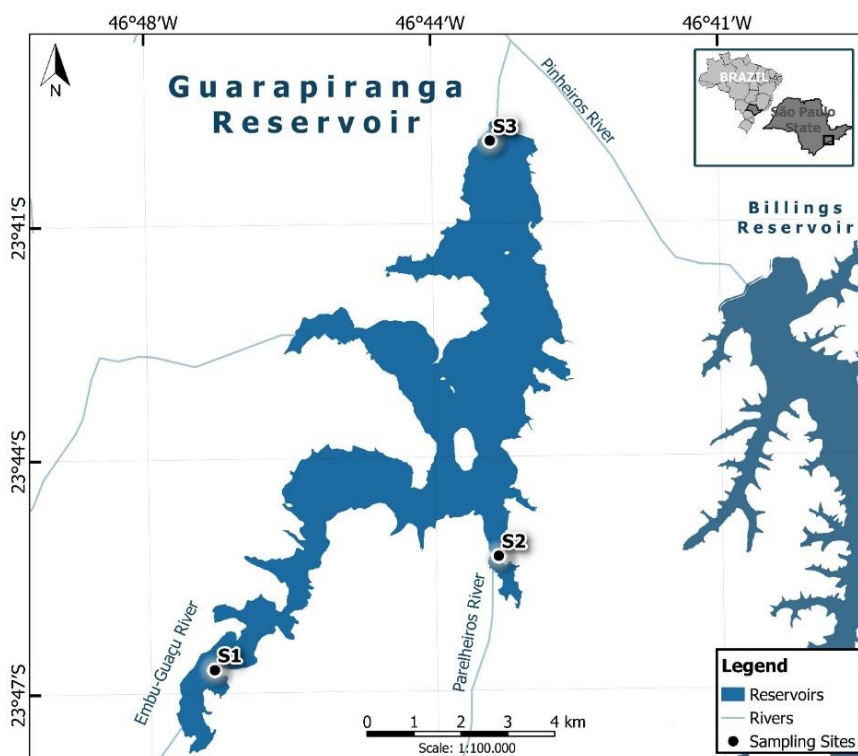


Figure 1: Sampling sites located at the Guarapiranga Reservoir.

3. RESULTS AND DISCUSSION

The results obtained for uranium and thorium concentrations in floating macrophytes species, as well as concentrations data reported in the literature [12], are presented in Table 2. The results obtained for lanthanide concentrations, as well as concentrations data reported in the literature [12] and for Guarapiranga soil values [13], are presented in Tables 3 and 4 for wet and dry season, respectively.

In general, the concentration levels for U, Th and lanthanides obtained were lower than those reported in similar study [12], for both campaigns (wet and dry seasons). *S. herzogii* and *S. molesta* species presented the highest concentration values for wet season, and *E. crassipes* specie presented the highest concentration values in the dry season. The same behavior was observed for U, Th and lanthanides in the analyzed macrophytes samples.

It should be noticed that Th, Nd, Eu, Tb, Yb and Lu concentrations are considered just informative values, because of the low concentrations of these elements in the studied matrix.

Table 2: Uranium and thorium concentrations (mg kg⁻¹) in macrophytes from the Guarapiranga Reservoir compared to data reported in the literature

Macrophytes species	Wet season				Dry season			
	Uranium		Thorium ^a		Uranium		Thorium ^a	
Site 01	Mean	Range	Mean	Range	Mean	Range	Mean	Range
<i>Eichhornia crassipes</i>	0.41	0.27 - 0.63	1.7	1.1 - 2.3	0.45	0.35 - 0.61	2.0	1.4 - 2.9
<i>Pistia stratiotes</i>	0.24	0.19 - 0.29	0.85	0.56 - 1.2	0.33	0.24 - 0.42	1.2	0.90 - 1.5
<i>Salvinia herzogii</i>	0.58	0.53 - 0.61	2.2	1.8 - 2.8	0.41	0.32 - 0.56	1.2	0.82 - 2.0
<i>Salvinia molesta</i>	0.47	0.38 - 0.53	1.9	1.3 - 2.3	0.43	0.33 - 0.60	1.3	0.99 - 1.4
Site 02								
<i>Eichhornia crassipes</i>	0.43	0.27 - 0.57	1.1	0.42 - 1.5	1.6	1.0 - 2.4	3.9	1.8 - 5.0
<i>Pistia stratiotes</i>	0.30	0.22 - 0.35	0.46	0.29 - 0.59	0.63	0.30 - 1.2	2.2	0.72 - 4.6
<i>Salvinia herzogii</i>	0.49	0.40 - 0.65	0.80	0.62 - 0.97	0.41	0.31 - 0.49	1.0	0.52 - 1.3
Site 03								
<i>Eichhornia crassipes</i>	0.28	0.23 - 0.34	0.55	0.41 - 0.62	0.78	0.57 - 1.1	2.5	1.2 - 4.6
<i>Pistia stratiotes</i>	0.25	0.23 - 0.28	0.43	0.32 - 0.51	0.47	0.31 - 0.81	1.1	0.43 - 2.2
<i>Salvinia herzogii</i>	0.31	0.22 - 0.47	0.54	0.26 - 0.99	0.61	0.45 - 0.90	1.9	0.78 - 3.4
Valitutto et al. [12]	Uranium		Thorium^a		Uranium		Thorium^a	
<i>Eichhornia crassipes</i>	1.53		7.93		1.53		7.93	
<i>Pistia stratiotes</i>	0.526		2.45		0.526		2.45	
<i>Salvinia auriculata</i>	1.22		4.52		1.22		4.52	

a. Informative values

3.1. Chondrite-normalized Rare Earth Elements Patterns

The results obtained for the lanthanides were normalized in relation to chondrite values as reference values, in order to better understand the REEs behavior and origin in the macrophytes. This normalization regarding to geological “reference” values can be a suitable tool to assess potential pollutant sources [14]. Chondrite-normalized rare earth elements patterns for macrophytes results and for Guarapiranga soil values [13] are presented in Fig. 2.

It can be seen that the lanthanides behavior in macrophytes samples are similar to those reported for Guarapiranga soil values [13] in both campaigns (wet and dry seasons), specially for dry season, showing an enrichment of the light REE (La to Sm), in contrast to the heavy REE (Eu to Lu). Chondrite-normalized rare earth elements patterns showed accumulation of REEs in *Salvinia* species for wet season and in *Eichhornia crassipes* for dry season.

In relation to data reported in the literature [12], the same pattern of accumulation of REEs in these macrophytes species was observed for dry season (*E. crassipes* > *Salvinia* > *Pistia stratiotes*).

3.2. Statistical Analysis

In order to assess the relationship among the studied chemical elements, an exploratory factorial analysis with principal components extraction was applied using the SPSS Statistics software (version 22 IBM), adopting the correlation matrix and varimax rotation.

The output showed that one component was extracted for each campaign (wet and dry seasons), indicating that the elements were grouped, basically, in one major group. The extracted component represents approximately 70% of data variance for wet season and 84% for dry season. These results indicate that the studied elements in macrophytes species of Guarapiranga Reservoir have the same origin, probably crustal.

4. CONCLUSIONS

In this study, the concentration levels of U, Th and lanthanides (La, Ce, Nd, Sm, Eu, Tb, Yb and Lu) were determined in four floating macrophytes species from Guarapiranga Reservoir. The diagrams normalized to chondrite values and statistical analysis showed that these elements have the same origin in this environment, probably natural. For U and Th results, concentration levels were in the range of those obtained in similar study, which indicates natural origin. Despite that, the increasing industrial use of REEs requires continuous monitoring of these elements in the aquatic environment.

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Table 3: Mean and range concentrations (mg kg⁻¹) of REEs in macrophytes from the Guarapiranga Reservoir (wet season)

Macrophytes species	La		Ce		Nd ^a		Sm		Eu ^a		Tb ^a		Yb ^a		Lu ^a	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Site 01																
<i>Eichhornia crassipes</i>	3.87	2.06 - 6.63	11	5.8 - 20	2.9	1.9 - 4.6	0.55	0.29 - 0.92	0.12	0.073 - 0.18	0.05	0.05 - 0.06	0.17	0.068 - 0.30	0.02	0.01 - 0.04
<i>Pistia stratiotes</i>	1.84	1.49 - 2.04	5.6	4.6 - 6.4	3.0	3.0	0.26	0.20 - 0.34	0.044	0.040 - 0.049	nd	nd	0.14	0.10 - 0.18	0.02	0.01 - 0.04
<i>Salvinia herzogii</i>	5.55	4.87 - 6.01	16	14 - 17	4.4	3.7 - 5.4	0.87	0.78 - 0.97	0.20	0.15 - 0.24	0.07	0.07	0.23	0.21 - 0.25	0.04	0.03 - 0.04
<i>Salvinia molesta</i>	3.91	3.24 - 4.70	11	10 - 14	4.4	2.9 - 5.7	0.59	0.45 - 0.72	0.13	0.077 - 0.18	0.08	0.07 - 0.09	0.21	0.18 - 0.23	0.03	0.02 - 0.05
Site 02																
<i>Eichhornia crassipes</i>	2.07	1.13 - 2.73	5.3	2.8 - 6.7	2.5	2.1 - 2.8	0.32	0.17 - 0.42	0.06	0.038 - 0.078	0.09	0.09	0.13	0.042 - 0.25	0.03	0.01 - 0.04
<i>Pistia stratiotes</i>	0.906	0.624 - 1.12	2.4	1.7 - 3.2	nd	nd	0.13	0.087 - 0.17	0.03	0.021 - 0.032	nd	nd	0.076	0.35 - 0.12	0.01	0.01 - 0.02
<i>Salvinia herzogii</i>	1.52	1.32 - 1.67	3.8	3.1 - 4.6	4.7	2.5 - 7.0	0.25	0.23 - 0.28	0.04	0.033 - 0.061	nd	nd	0.12	0.073 - 0.20	0.02	0.01 - 0.02
Site 03																
<i>Eichhornia crassipes</i>	1.38	1.24 - 1.48	3.2	2.9 - 3.6	1.8	1.2 - 2.1	0.19	0.17 - 0.20	0.04	0.035 - 0.046	nd	nd	0.085	0.050 - 0.12	0.02	0.01 - 0.02
<i>Pistia stratiotes</i>	1.16	0.883 - 1.42	2.8	2.0 - 3.3	nd	nd	0.17	0.15 - 0.20	0.03	0.023 - 0.038	nd	nd	0.078	0.049 - 0.11	0.01	0.01
<i>Salvinia herzogii</i>	1.61	0.885 - 3.03	3.7	1.9 - 7.3	2.0	0.94 - 3.1	0.27	0.13 - 0.52	0.06	0.025 - 0.13	0.15	0.15	0.12	0.036 - 0.28	0.02	0.01 - 0.04
Valitutto et al. [12]																
<i>Eichhornia crassipes</i>		18		59		17		3.2		0.72		0.43		0.99		-
<i>Pistia stratiotes</i>		4.7		13		3.6		0.74		0.21		0.08		0.23		-
<i>Salvinia auriculata</i>		4.7		26		6.1		1.2		0.35		0.14		0.36		-
Guarapiranga soil values [13]		50		130		47		8.0		1.09		1.3		4.2		0.54

a. Informative values

*nd = not determined

Table 4: Mean and range concentrations (mg kg⁻¹) of REEs in macrophytes from the Guarapiranga Reservoir (dry season)

Macrophytes species	La		Ce		Nd ^a		Sm		Eu ^a		Tb ^a		Yb ^a		Lu ^a	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Site 01																
<i>Eichhornia crassipes</i>	4.75	3.69 - 6.44	14	8.8 - 19	4.7	3.2 - 6.5	0.68	0.58 - 0.86	0.15	0.090 - 0.22	0.1	0.06 - 0.2	0.30	0.22 - 0.44	0.04	0.03 - 0.07
<i>Pistia stratiotes</i>	2.93	2.34 - 3.89	8.0	6.0 - 11	2.4	2.2 - 2.5	0.44	0.35 - 0.57	0.087	0.074 - 0.11	0.06	0.02 - 0.09	0.15	0.11 - 0.21	0.02	0.01 - 0.03
<i>Salvinia herzogii</i>	3.48	2.30 - 4.94	9.4	6.4 - 14	2.6	2.1 - 3.3	0.57	0.36 - 0.82	0.12	0.082 - 0.19	0.03	0.03	0.19	0.10 - 0.28	0.03	0.02 - 0.05
<i>Salvinia molesta</i>	4.67	3.00 - 7.57	11	8.1 - 16	3.5	2.7 - 4.2	0.81	0.52 - 1.4	0.15	0.11 - 0.20	0.2	0.06 - 0.3	0.48	0.12 - 1.15	0.07	0.03 - 0.15
Site 02																
<i>Eichhornia crassipes</i>	10.7	5.15 - 16.7	26	12 - 43	8.2	3.2 - 15	1.7	0.86 - 2.9	0.32	0.16 - 0.53	0.2	0.14 - 0.3	1.1	0.35 - 2.26	0.2	0.05 - 0.3
<i>Pistia stratiotes</i>	5.07	2.31 - 9.89	12	5.2 - 22	4.1	2.6 - 5.6	0.73	0.25 - 1.4	0.14	0.053 - 0.25	0.09	0.04 - 0.1	0.17	0.044 - 0.36	0.03	0.02 - 0.06
<i>Salvinia herzogii</i>	3.29	1.35 - 5.52	8.7	3.7 - 15	3.3	0.54 - 6.6	0.53	0.19 - 0.97	0.10	0.036 - 0.19	0.03	0.03	0.20	0.13 - 0.28	0.03	0.01 - 0.06
Site 03																
<i>Eichhornia crassipes</i>	7.33	3.87 - 12.4	16	8.5 - 27	6.5	3.0 - 11	1.2	0.73 - 1.9	0.26	0.17 - 0.41	0.2	0.1 - 0.2	0.45	0.29 - 0.75	0.08	0.05 - 0.1
<i>Pistia stratiotes</i>	2.77	1.98 - 4.08	6.3	4.1 - 10	2.2	1.6 - 3.3	0.48	0.33 - 0.75	0.11	0.072 - 0.17	0.08	0.03 - 0.2	0.41	0.10 - 0.73	0.05	0.01 - 0.1
<i>Salvinia herzogii</i>	4.87	1.84 - 8.56	11	3.9 - 21	4.4	1.1 - 8.2	0.86	0.33 - 1.4	0.17	0.083 - 0.27	0.2	0.06 - 0.3	0.51	0.30 - 0.79	0.09	0.03 - 0.1
Valitutto et al. [12]																
<i>Eichhornia crassipes</i>	18		59		17		3.2		0.72		0.43		0.99		-	
<i>Pistia stratiotes</i>	4.7		13		3.6		0.74		0.21		0.08		0.23		-	
<i>Salvinia auriculata</i>	4.7		26		6.1		1.2		0.35		0.14		0.36		-	
Guarapiranga soil values [13]	50		130		47		8.0		1.09		1.3		4.2		0.54	

a Informative values

*nd = not determined

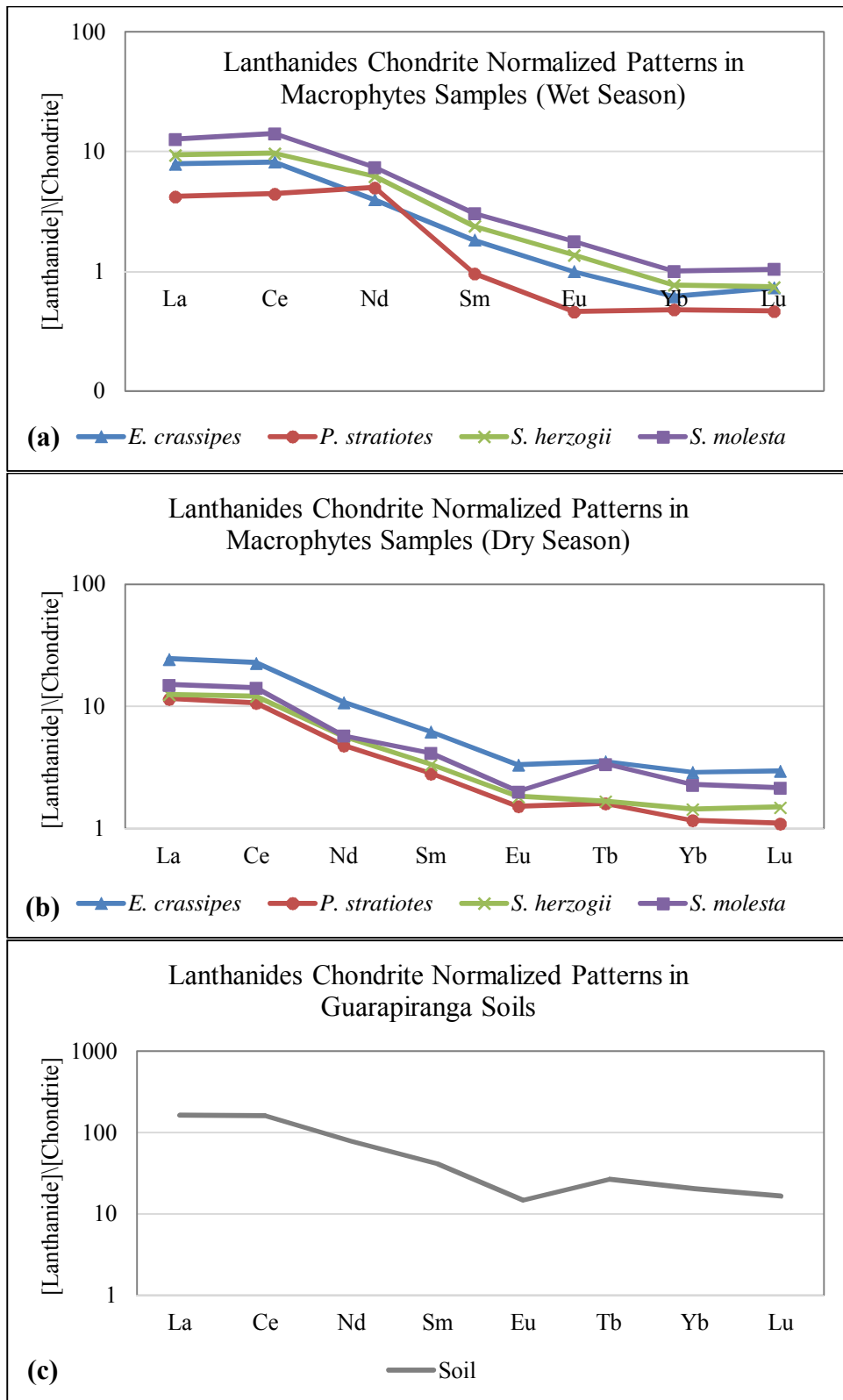


Figure 2: (a) Chondrite normalized REEs patterns in four floating aquatic macrophytes species from the Guarapiranga Reservoir (wet season); (b) Chondrite normalized REEs patterns in four floating aquatic macrophytes species from the Guarapiranga Reservoir (dry season); (c) Chondrite normalized REEs patterns in Guarapiranga soils [13]

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